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Evaluation of EPA (Environmental Protection Agency) Method 8120 for Determination of Chlorinated Hydrocarbons in Environmental Samples

Acurex Corp., Mountain View, CA

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The misuse of Chlorohydrocarbon and improper disposals practices have resulted in polluting various watersheds

16. ABSTRACT

Method 8120 of EPA Manual SW-846 has been evaluated in a single-laboratory study. Modifications made to the current method include expansion of the list of target compounds from 15 to 22; replacement of the packed gas chromatographic columns with 2 megabore fused-silica open tubular columns; modification of the Florisil cleanup procedure to allow quantitative recovery of 20 of the 22 target compounds; and development of a procedure that uses 1-g Florisil disposable cartridges and gives quantitative recovery of all 22 target compounds from all matrices tested. The revised method was tested with a variety of sample matrices.

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ENVIRONMENTAL ANALYSIS

EPA/600/J-89/096

Evaluation of EPA Method 8120 for Determination of Chlorinated Hydrocarbons in Environmental Samples

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Method 8120 of EPA Manual SW-846 has been evaluated in a single-laboratory study. Several modifications made to the current method were implemented to allow determination of selected chlorinated hydrocarbons in complex environmental samples. The 2 packed gas chromatographic columns specified in Method 8120 were replaced with 2 megabore fused-silica open tubular columns chemically bonded with trifluoropropylmethyl siloxane and polyethylene glycol, respectively. The list of target compounds was expanded from 15 to 22 to include all possible trichlorobenzenes, tetrachlorobenzenes, and hexachlorocyclohexane (BHC) isomers. The Florisil cleanup procedure was modified to allow quantitative recovery of 20 of the 22 target compounds. A procedure that uses 1 g Florisil disposable cartridges and hexane–acetone (9:1) eluant was developed. This latter procedure gives quantitative recovery of all 22 target compounds from all matrixes tested. The revised method was tested with a variety of sample matrixes. Detection limits for water samples ranged from 1.4 ng/L for hexachlorobutadiene to 1300 ng/L for 2-chloronaphthalene; detection limits for 15 compounds were below 40 ng/L. Because of background contamination, detection limits for soil and sediment samples need to be determined on a case-by-case basis.

The chlorinated hydrocarbons discussed in this paper include the chlorinated benzenes (11 compounds), benzyl chloride, benzal chloride, benzotrichloride, the 4 hexachlorocyclohexane (BHC) isomers, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, and 2-chloronaphthalene. The occurrence of these compounds in the environment seems to be related to their production (e.g., 200 000 metric tons of chlorinated benzenes were produced in the United States in 1978) as well as to their uses (1). Misuse of these compounds and improper disposal practices have resulted in contamination of various watersheds (2–4).

Some of these chlorinated hydrocarbons have been determined in environmental samples by gas chromatography using electron capture detectors (5–8), Hall electrolytic conductivity detectors (9, 10), and photoionization detectors (11, 12), and by mass spectrometry (8, 13–16). Lee et al. (8) used a mass selective detector in the selective ion monitoring mode to improve detector sensitivity, and Crow et al. (16) used negative ion chemical ionization mass spectrometry for qualitative and quantitative determination of the chlorinated hydrocarbons. To increase the sensitivity of the electron capture detector for those chlorinated hydrocarbons with few chlorine atoms, Miller and Grimsrud (17) proposed doping the carrier gas with oxygen up to 3.5 parts per thousand. A general approach to the fractionation and class determination of complex mixtures of chlorinated hydrocarbons was reported by Albro and Parker (18), and determination in foods and in human adipose tissues was reported by Yurawecz and Puma (19) and LeBel and Williams (20), respectively. However, no literature reports could be retrieved that deal with the determination of all 22 compounds listed in Table 1.

Most EPA standard methods employ packed column gas chromatography (GC) with confirmation of compounds on columns of different polarity. Furthermore, cleanup of sample extracts prior to GC analysis is not always specified, or, if specified, information is insufficient in the method about the compound's elution pattern and recovery from complex matrixes. Therefore, methods require not only improvement but also evaluation with "real world" samples.

The purpose of the present study was to improve sample extraction, extract cleanup, and GC determination steps in the current EPA Method 8120 (6), and then to determine applicability of the revised method to complex environmental matrixes.

Problems with Method 8120 include the following: (*1*) The primary column specified in the method, a 1.8 m × 2 mm id glass column packed with 1% SP-1000 on 100/120 mesh Supelcoport, must be operated at 2 temperatures (65 and 150°C) to chromatograph 8 of the 15 target compounds listed. No information is included in the method about the other 7 compounds.

(*2*) The confirmatory column specified in the method, a 1.8 m × 2 mm id glass column packed with 1.5% OV-1/2.4% OV-225 on 80/100 mesh Supelcoport, must be operated at 3 temperatures (75, 100, and 165°C) to chromatograph 9 of the 15 target compounds.

(*3*) The method does not specify isomers for trichlorobenzenes, tetrachlorobenzenes, and BHCs.

(*4*) Detection limits are given for only 9 of the 15 target compounds listed.

(*5*) Surrogate compounds must be added to the sample matrix prior to extraction, yet no compounds are recommended for this purpose. Likewise, internal standards are required whenever internal standard calibration is used for quantification, yet none are recommended.

(*6*) Extracts are cleaned up according to Method 3620, yet no recovery data are included to indicate that the target compounds are recovered quantitatively from the Florisil column by elution with petroleum ether.

The current method lists only 1,2,4-trichlorobenzene of the trichlorobenzene isomers and does not specify any isomers for tetrachlorobenzene or BHC, so the list of target compounds in the revised method was expanded to include all the trichlorobenzenes, tetrachlorobenzenes, and BHC isomers. The 22 compounds used in the evaluation study are shown in Table 1.

Since analyses with packed columns did not give satisfactory results, 5 fused-silica open tubular columns were evaluated for their suitability for this type of compounds. The results of this evaluation were published elsewhere (21). The GC procedure selected for incorporation in revised Method 8120 was subjected to ruggedness testing.

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Table 1. Compounds listed in revised EPA Method 8120

Compound	Chemical Abstracts Service Registry No.	Abbreviation used in text and figures
Benzal chloride	98-87-3	BENZALCL
Benzotrichloride	98-07-7	BENZOTRICL
Benzyl chloride	100-44-7	BENZYLCL
2-Chloronaphthalene	91-58-7	CN-2
1,2-Dichlorobenzene	95-50-1	DCB 1,2
1,3-Dichlorobenzene	541-73-1	DCB 1,3
1,4-Dichlorobenzene	106-46-1	DCB 1,4
Hexachlorobenzene	118-74-1	HCB
Hexachlorobutadiene	87-68-3	HCBU
alpha-Hexachlorocyclohexane (alpha-BHC)	319-84-6	ALPHA-BHC
beta-Hexachlorocyclohexane (beta-BHC)	319-85-7	BETA-BHC
gamma-Hexachlorocyclohexane (gamma-BHC)	58-89-9	GAMMA-BHC
delta-Hexachlorocyclohexane (delta-BHC)	319-86-8	DELTA-BHC
Hexachlorocyclopentadiene	77-47-4	HCCP
Hexachloroethane	67-72-1	HCE
Pentachlorobenzene	608-93-5	QCB
1,2,3,4-Tetrachlorobenzene	634-66-2	TETCB 1,2,3,4
1,2,4,5-Tetrachlorobenzene	95-94-2	TETCB 1,2,4,5
1,2,3,5-Tetrachlorobenzene	634-90-2	TETCB 1,2,3,5
1,2,4-Trichlorobenzene	120-82-1	TRICB 1,2,4
1,2,3-Trichlorobenzene	87-61-6	TRICB 1,2,3
1,3,5-Trichlorobenzene	108-70-3	TRICB 1,3,5

The use of commercially available disposable Florisil cartridges for sample extract cleanup was evaluated to simplify and standardize the Florisil cleanup procedure. Possible interferences from other chlorinated compounds such as chlorinated phenols, toluenes, xylenes, polynuclear aromatic hydrocarbons, and others were investigated.

Six bromoaromatic and 35 chloroaromatic compounds were tested for their suitability as internal standards and as surrogates, respectively. Retention times for several of these compounds on the columns of interest do not interfere with those of the target compounds.

Finally, conditions for sample preservation were investigated, method detection limits were established, and the modified method was tested on a variety of sample matrixes. The final evaluation of the revised method was conducted at 3 target analyte concentrations, each analyzed in triplicate.

Experimental

Apparatus and Materials

(a) *Glassware.*—Separatory funnel, 2000 mL, with Teflon stopcock; glass drying column, 21 cm × 45 mm id, plugged with glass wool; Kuderna-Danish evaporative flask, 500 mL, with 10 mL graduated concentrator tube and 3-ball macro Snyder column; wide-mouth amber glass bottle, 500 mL, with Teflon-lined screw cap; glass cleanup column, 50 cm × 20 mm id, with 200 mL reservoir and Teflon stopcock.

(b) *Water bath.*—With concentric ring cover; heated to 98 ± 2°C.

(c) *Sonicator.*—Model W-375 (Heat Systems-Ultrasonics, Inc., Farmingdale, NY 11735), or equivalent, with 20 kHz ultrasonic convertor Model C3, or equivalent.

(d) *Gas chromatograph.*—Equipped with ^{63}Ni constant-current pulsed-frequency electron capture detector, autosampler, stripchart recorder, and integrator. Operating conditions: injection port 220°C; detector 250°C; helium carrier gas at 10 mL/min; nitrogen detector makeup gas at 40 mL/min; on-column injection.

(e) *GC columns.*—(*1*) DB-210 fused-silica open tubular column, 30 m × 0.53 mm id (J & W Scientific Inc., Folsom, CA 95630), film thickness 1 μm. Temperature program: initial 65°C, programmed at 4°/min to 175°C, final hold 20 min; (*2*) DB-WAX fused-silica open tubular column, 30 m × 0.53 mm id (J & W Scientific Inc.), film thickness 1 μm. Temperature program: initial 60°C, programmed at 4°/min to 170°C, final hold 30 min.

(f) *Balance.*—Analytical, capable of accurately weighing to nearest 0.0001 g.

Reagents

(a) *Solvents.*—Methylene chloride, hexane, isooctane, petroleum ether, acetone; all pesticide grade, distilled in glass.

(b) *Sodium sulfate.*—ACS grade, granular anhydrous. Purify by heating 4 h at 400°C in shallow tray.

(c) *Florisil.*—J. T. Baker, Lot No. 442707, 60/80 mesh, activated at 130°C for at least 16 h before use. Florisil was calibrated by lauric acid method (22).

(d) *Disposable Florisil cartridges.*—Supelclean SPE tubes consisting of serological-grade polypropylene tubes, 6 mL volume, packed each with 1 g LC-Florisil (40 μm particles, 60 Å pores) held between polyethylene frits (20 μm pores).

(e) *Standards.*—High purity benzyl chloride, 2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, hexachlorobutadiene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, hexachlorocyclopentadiene, hexachloroethane, and 1,2,4-trichlorobenzene (U.S. EPA Pesticides and Industrial Chemicals Repository). Benzal chloride, 1,2,3,5-tetrachlorobenzene and the brominated compounds (Aldrich Chemical Co., Inc., Milwaukee, WI 53201). Other compounds listed in Table 1 were obtained from Ultra Scientific, Inc. (Hope, RI 02831). A stock solution of each test compound was prepared in pesticide-grade isooctane at 1 mg/mL, and working calibration standards were prepared in isooctane by serial dilution of composite stock solution prepared from individual stock solutions. α,α′-Dibromo-*m*-xylene was used as internal standard.

Samples

Sandy loam soil (sample A) was obtained from Soils Inc. (Puyallup, WA 98371) and had the following physicochemical characteristics: pH 5.9–6.0; 89% sand, 7% silt, 4% clay; cation exchange capacity 7 meq/100 g; total organic carbon content 1290 ± 185 mg/kg.

Sediment sample (sample B) was of unknown origin, contaminated with petroleum hydrocarbons.

Detroit River sediment (sample C) collected from Detroit River at Station 30CR was reportedly highly contaminated with polychlorinated biphenyls (PCBs), chloronaphthalenes, and terphenyls (1–3 ppm levels).

Bloody Run Creek sediment (sample D) was a grab sample collected from creek downstream of Love Canal dump site (102nd St). Jaffe and Hites (23) reported ppm concentrations of dichloro(trifluoromethyl)benzophenone, dichloro-(trifluoromethyl)difluoro-diphenylmethane, and various chlorinated trifluoromethyl-substituted biphenyls.

NIST Standard Reference Materials included SRM 1575, SRM 1645, SRM 1572, SRM 1632a, and SRM 1633a (samples E, F, G, H, and I, respectively).

Love Canal soil (sample J) was obtained from Environmental Research Center, University of Nevada.

Table 2. Gas chromatographic retention times for compounds investigated and proposed for incorporation in EPA Method 8120

Compound No.	Compound	Retention time, min DB-210[a]	DB-WAX[b]
1	Benzal chloride	6.86[d]	15.59
2	Benzotrichloride	7.85	15.10
3	Benzyl chloride	4.59	10.42[f]
4	2-Chloronaphthalene	13.45	22.70[g]
5	1,2-Dichlorobenzene	4.44	9.72
6	1,3-Dichlorobenzene	3.66	7.95
7	1,4-Dichlorobenzene	3.80	8.68
8	Hexachlorobenzene	19.23	27.44
9	Hexachlorobutadiene	5.77	10.08
10	alpha-BHC	22.21	36.86
11	beta-BHC	25.54	47.46
12	gamma-BHC	24.07	46.24
13	delta-BHC	26.16	31.33
14	Hexachlorocyclopentadiene	8.86	—[c]
15	Hexachloroethane	3.35	8.33
16	Pentachlorobenzene	14.86	22.70[g]
17	1,2,3,4-Tetrachlorobenzene	11.90	20.33
18	1,2,4,5-Tetrachlorobenzene	10.18[e]	17.28
19	1,2,3,5-Tetrachlorobenzene	10.18[e]	17.00
20	1,2,4-Trichlorobenzene	6.86[d]	13.57
21	1,2,3-Trichlorobenzene	8.14	15.62
22	1,3,5-Trichlorobenzene	5.45	10.42[f]

[a] GC conditions are as follows: 30 m × 0.53 mm id DB-210 fused-silica open tubular column; temperature program: 65 to 175°C (hold 20 min) at 4°/min; injector temperature 220°C; detector temperature 250°C; carrier gas is helium at 10 mL/min and makeup gas is nitrogen at 40 mL/min.

[b] GC conditions are as follows: 30 m × 0.53 mm id DB-WAX fused-silica open tubular column; temperature program: 60 to 170°C (hold 30 min) at 4°/min; injector temperature 200°C; detector temperature 230°C; carrier gas is helium at 10 mL/min and makeup gas is nitrogen at 40 mL/min.

[c] Compound decomposes on column.

[d,e,f,g] These compound pairs cannot be separated on the respective columns.

Figure 1. GC/ECD chromatogram of Method 8120 compounds analyzed on 30 m × 0.53 mm id DB-210 fused-silica open tubular column. GC operating conditions are as follows: 65 to 175°C (hold 20 min) at 4°/min; injector temperature 220°C; detector temperature 250°C; helium carrier gas at 10 mL/min; nitrogen makeup gas at 40 mL/min. See Table 2 for peak identification. Compound concentrations range from 0.1 to 20 μg/mL.

PCB-contaminated soil (sample K) was obtained from William Budde, EPA-Cincinnati.

San Francisco Bay water (pH 8.0) was collected near Leslie Salt Hill (off Seaport Blvd, South San Francisco, CA). Sample was refrigerated at 4°C until analyzed.

Leachate samples were prepared from Detroit River sediment and Bloody Run Creek sediment as follows: 100 g (net weight) of each sediment was mixed with 1600 mL deionized water, adjusted to pH 5.2 with 0.5N acetic acid, and shaken 24 h on mechanical shaker. Details of procedure are given in Method 1310 of SW-846 Methods Manual (1). Each leachate was filtered through 0.45 μm Millipore filter (Fisher Scientific, Pittsburgh, PA 15219) prior to extraction with methylene chloride.

Sample Preparation

From 800–1000 mL liquid samples were spiked with 3 surrogate compounds, α,2,6-trichlorotoluene, 1,4-dichloronaphthalene, and 2,3,4,5,6-pentachlorotoluene, and extracted at neutral pH in a separatory funnel with 60 mL methylene chloride. Extraction was repeated twice. Extracts were combined, dried by passing through column of anhydrous sodium sulfate, and concentrated in Kuderna-Danish evaporator to <10 mL. Hexane (50 mL) was added to concentrate, and volume was reduced to <10 mL. Further concentration to 1 or 2 mL was performed by nitrogen blowdown evaporation using gentle stream of pure nitrogen (99.999% purity).

Ten 35 g solid samples were spiked with 22 target compounds in wide-mouth bottle. Moisture was removed by adding anhydrous sodium sulfate that had been preheated 4 h at 400°C. Samples were extracted with 100 mL methylene chloride–acetone (1:1) by sonicating 3 min. Extraction was repeated twice, each time for 3 min and with fresh 100 mL portions of methylene chloride–acetone (1:1). Extracts were combined, filtered through Whatman No. 41 paper, dried by passing them through column of anhydrous sodium sulfate, and concentrated in Kuderna-Danish evaporator to <10 mL. Hexane (50 mL) was added to concentrate, and volume was reduced to 10 mL. Further concentration to 2 mL was performed by nitrogen blowdown evaporation using gentle stream of pure nitrogen (99.999% purity).

Florisil Cleanup

Florisil (60/80 mesh) was activated ≥16 h at 130°C before use. Its activity was determined by using lauric acid method (22). Glass columns (50 cm × 20 mm id) were packed with 12.3 g activated Florisil and prewashed with 200 mL petroleum ether before use. Target compounds were eluted from Florisil with 200 mL petroleum ether and 200 mL diethyl ether–petroleum ether (1:1). All fractions were concentrated to 10 mL by Kuderna-Danish evaporation.

When Florisil disposable cartridges (Supelco, Inc.) containing LC-Florisil (40 μm particles, 60 Å pores) were used, each cartridge was prewashed with 4 mL pesticide-grade hexane prior to use. Each cartridge was eluted with 5 mL hexane–acetone (9:1). Eluate was concentrated to 1 mL prior to gas chromatographic analysis.

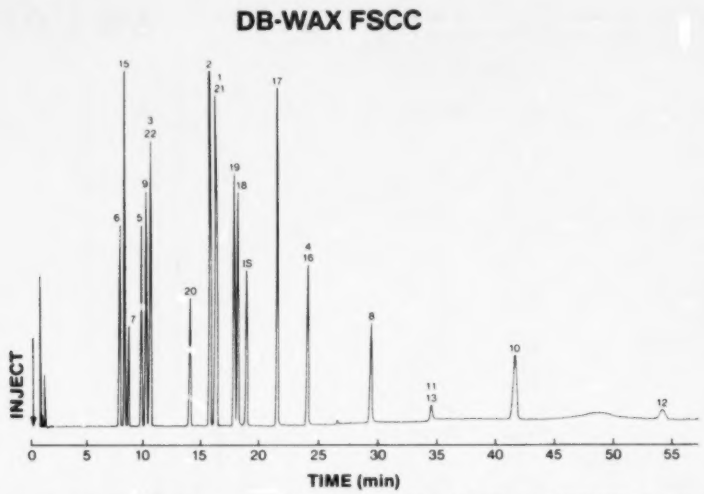

Figure 2. GC/ECD chromatogram of Method 8120 compounds analyzed on 30 m × 0.53 mm id DB-WAX fused-silica open tubular column. GC operating conditions are as follows: 60 to 170°C (hold 30 min) at 4°/min; injector temperature 200°C; detector temperature 230°C; helium carrier gas at 10 mL/min; nitrogen makeup gas at 40 mL/min. See Table 2 for peak identification. Compound concentrations range from 0.1 to 20 μg/mL.

Gas Chromatography

GC operation was set up as described under Apparatus and Materials **(d)**. GC system was calibrated by using external standard technique. Five-level calibration was performed before samples were analyzed. Single-level calibrations were performed daily, before each sequence of analyses and after every 8 h of continuous operation to verify linearity of detector response. One μL calibration standards or samples were injected by using autosampler. Every sample extract, method blank, or QC sample was spiked with α,α′-dibromo-*m*-xylene (internal standard) prior to injection into GC. Peak areas were recorded. When peak areas exceeded linear range of method, extract was diluted and reanalyzed.

Sample preservation studies were carried out on water samples by spiking fourteen 1 L deionized water samples with target compounds at one concentration and by storing

Table 3. Percent recoveries of target compounds from selected solid matrixes

Compound	Added, μg/mL extract	Matrix A	B	C[a]	D[a]	E	F	G	H	I
Benzal chloride[b]	2.0	—[c]	102	113	104	95	85	96	94	103
Benzotrichloride	2.0	58	84	100	94	76	80	90	75	82
Benzyl chloride	10	96	96	97	91	83	84	112	85	96
2-Chloronaphthalene	20	90	78	94	85	100	—[c]	84	80	78
1,2-Dichlorobenzene	10	98	84	97	100	79	67	80	73	83
1,3-Dichlorobenzene	10	86	71	122	57	68	57	67	58	69
1,4-Dichlorobenzene	10	93	78	111	87	65	59	120	59	39
Hexachlorobenzene	0.1	99	76	90	181	78	—[c]	61	57	78
Hexachlorobutadiene	0.1	83	65	80	85	59	60	57	54	65
alpha-BHC	1.0	102	98	98	99	93	99	99	98	101
gamma-BHC	1.0	105	98	98	99	91	107	101	100	102
beta-BHC	1.0	95	85	92	96	65	105	85	90	97
delta-BHC	1.0	110	114	125	99	114	73	98	75	100
Hexachlorocyclopentadiene	0.1	36	31	—[c]	83	46	23	123	28	35
Hexachloroethane	0.1	88	79	93	82	72	70	78	70	76
Pentachlorobenzene	0.1	90	76	115	107	85	70	58	74	71
1,2,3,4-Tetrachlorobenzene	1.0	104	80	65	115	78	—[c]	69	75	83
1,2,4,5-Tetrachlorobenzene[c]	2.0	86	70	125	77	76	59	50	63	61
1,2,3,5-Tetrachlorobenzene[c]	2.0	86	70	125	77	76	59	50	63	61
1,2,4-Trichlorobenzene[b]	2.0	—[c]	102	113	104	95	85	96	94	103
1,2,3-Trichlorobenzene	1.0	103	89	113	110	81	74	70	73	91
1,3,5-Trichlorobenzene	1.0	92	75	—[c]	59	67	63	46	59	68
Surrogate recovery, %:										
α,2,6-Trichlorotoluene	1.0	106	82	101	105	98	—[d]	88	104	89
1,4-Dichloronaphthalene	10	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]	78	48	—[d]
2,3,4,5,6-Pentachlorotoluene	1.0	87	70	92	126	86	—[d]	88	75	65

[a] Spiking level is one-thousandfold higher than shown in this table because of high native chlorinated hydrocarbons levels in these materials.
[b,c] These pairs cannot be separated on the DB-210 column.
[d] Not able to determine recovery because of matrix interference.

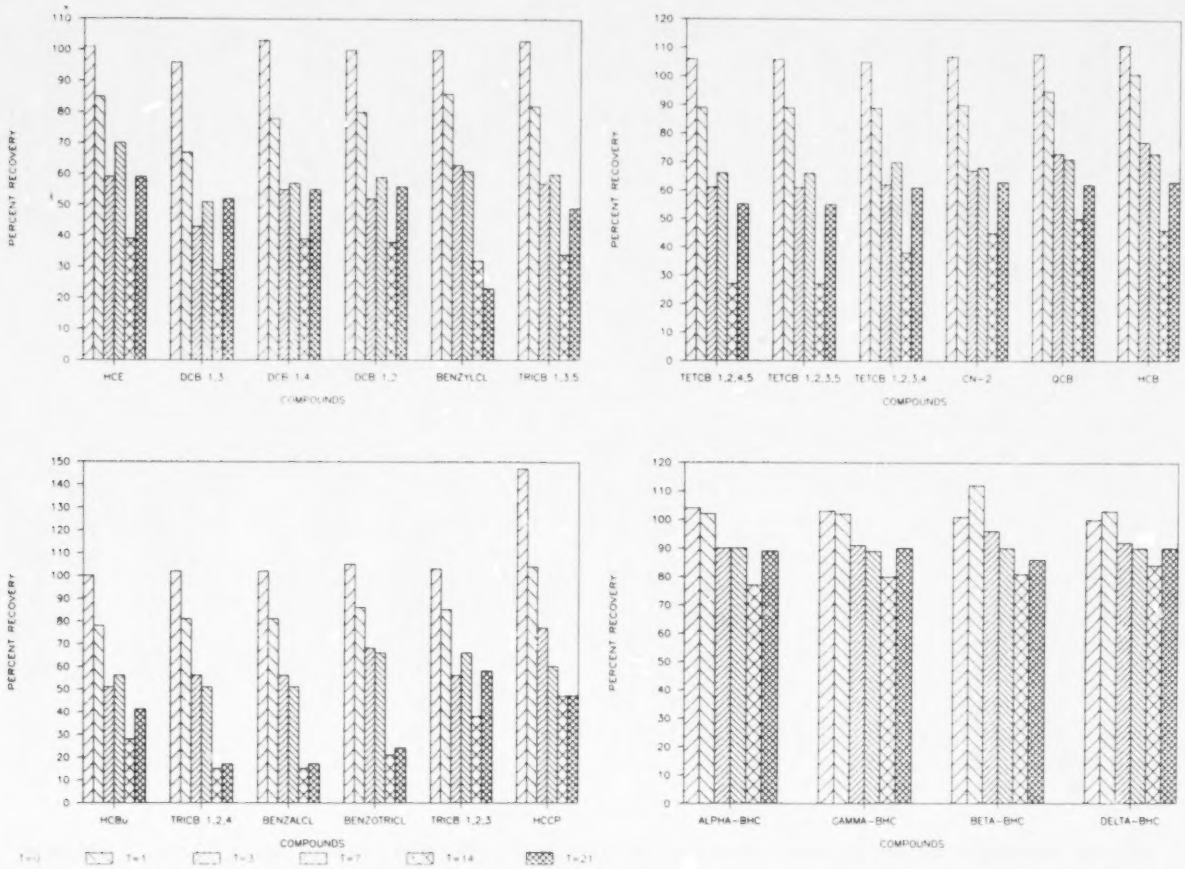

Figure 3. Recovery of Method 8120 compounds as function of time at pH 7 (time events are T = 0 days, T = 1 day, T = 3 days, T = 7 days, T = 14 days, T = 21 days).

up to 21 days at 4°C. Two samples were extracted immediately; other samples were removed in duplicate on days 1, 3, 7, 10, 14, and 21 and analyzed for 22 target compounds. In addition, six 1 L samples were spiked with target compounds at one concentration and adjusted to pH 2 with 6N H_2SO_4. Two samples were extracted immediately; other samples were stored at 4°C. Duplicates were removed on days 7 and 14 and analyzed. This experiment was also conducted with spiked deionized water samples adjusted to pH 9 with 10N NaOH. The spiking levels of the 22 compounds were as follows: 0.2 μg/L for hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, pentachlorobenzene, and hexachlorobenzene; 2.0 μg/L for trichlorobenzenes, tetrachlorobenzenes, benzal chloride, benzotrichloride, and BHC isomers; 20 μg/L for dichlorobenzenes and benzyl chloride, and 40 μg/L for 2-chloronaphthalene.

Results and Discussion

Gas Chromatography

A few attempts were made to chromatograph the 22 target compounds under temperature-programmed conditions by using one of the packed columns specified in the method. Separation of the more volatile chlorinated benzenes on the packed column was unacceptable, and the background from column bleed was excessive. Consequently, no further attempts were made to optimize the conditions for analysis on the packed column. Several fused-silica open tubular columns were evaluated for their suitability for analysis of the target compounds (21). Two of these columns, a 30 m × 0.53 mm id DB-210 fused-silica open tubular column and a 30 m × 0.53 mm id DB-WAX fused-silica open tubular column, were proposed for incorporation in the revised method as the primary and confirmatory columns, respectively. Table 2 summarizes the retention times of the 22 target compounds on these 2 columns. Figures 1 and 2 present GC/ECD chromatograms of a composite standard of the 22 target compounds analyzed on the DB-210 and DB-WAX columns, respectively.

Of 6 bromoaromatics tested for suitability as internal standards, α,α′-dibromo-*m*-xylene was best suited, with retention times of 18.41 min for the DB-210 column and 35.94 min for the DB-WAX column. 1,3,5-Tribromobenzene (11.67 min on the DB-210 column and 22.60 min on the DB-WAX column) was also suitable, however, that compound coeluted with α,2,6-trichlorotoluene, and was incompletely separated from 1,2,3,4-tetrachlorobenzene when the latter was present at >1 ng/μL. Of 35 chlorinated aromatics tested for suitability as surrogates, α,2,6-trichlorotoluene, 1,4-dichloronaphthalene, and 2,3,4,5,6-pentachlorotoluene were recommended. Their retention times on the DB-210 column are 12.96, 17.43, and 18.96 min, respectively, and on the DB-WAX column 23.34, 26.33, and 27.66 min, respectively.

Florisil Cleanup

Cleanup of sample extracts was performed initially as described in EPA Method 3620 (24). Florisil (60/80 mesh), activated prior to use for ≥16 h at 130°C, was used in this

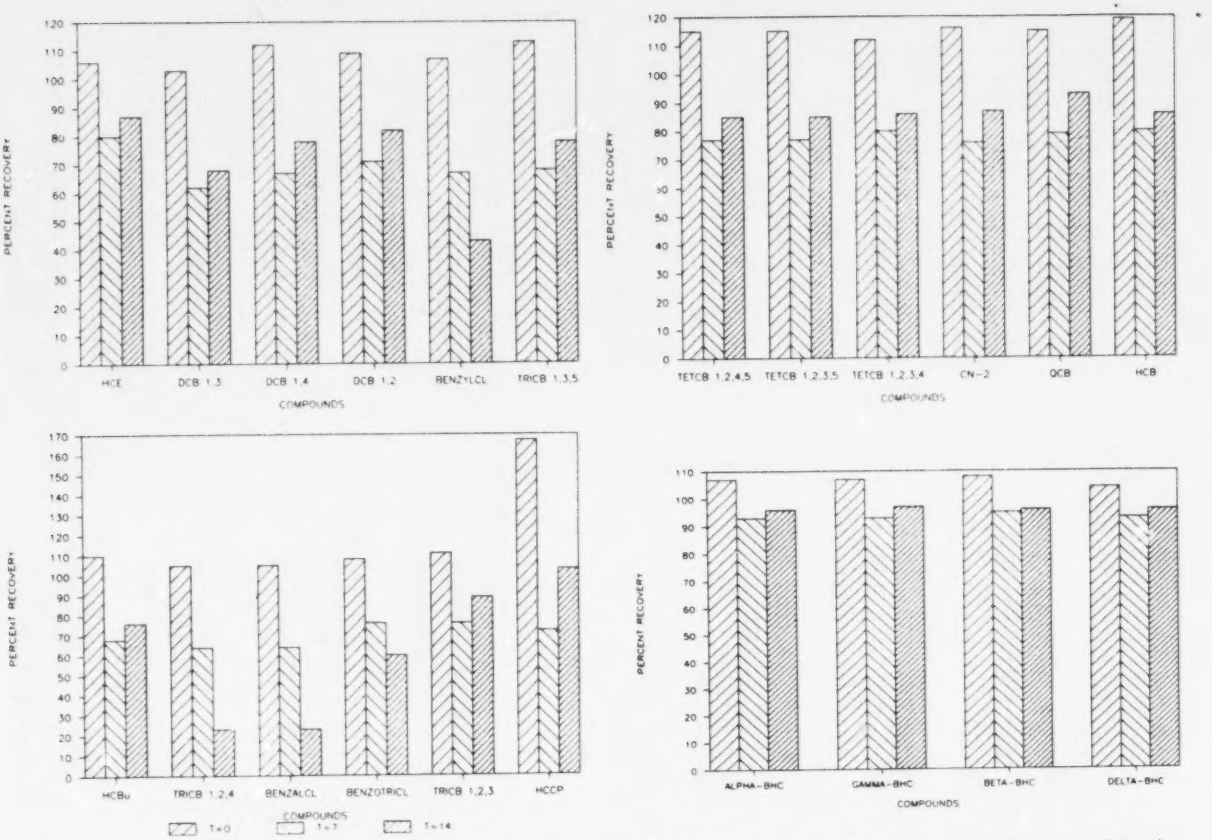

Figure 4. Recovery of Method 8120 compounds as a function of time at pH 2 (time events are T = 0 days, T = 7 days, T = 14 days).

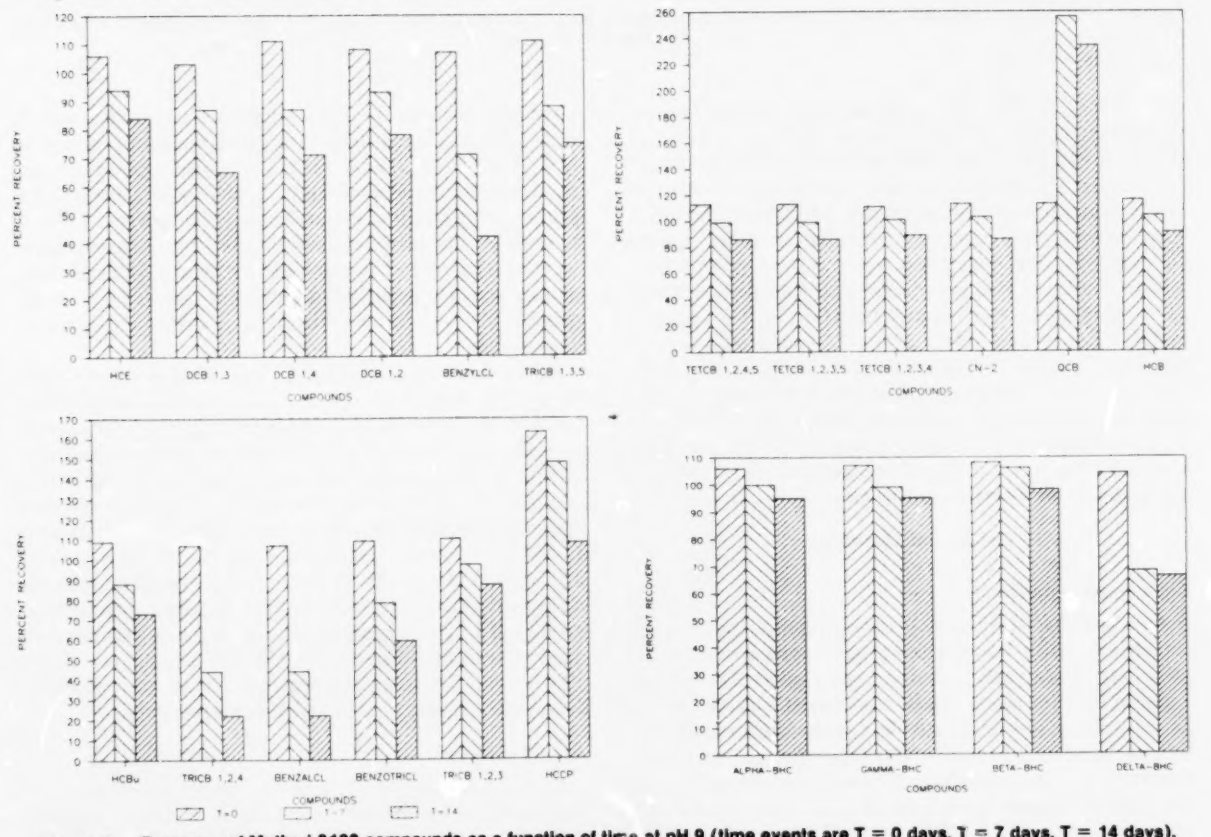

Figure 5. Recovery of Method 8120 compounds as a function of time at pH 9 (time events are T = 0 days, T = 7 days, T = 14 days).

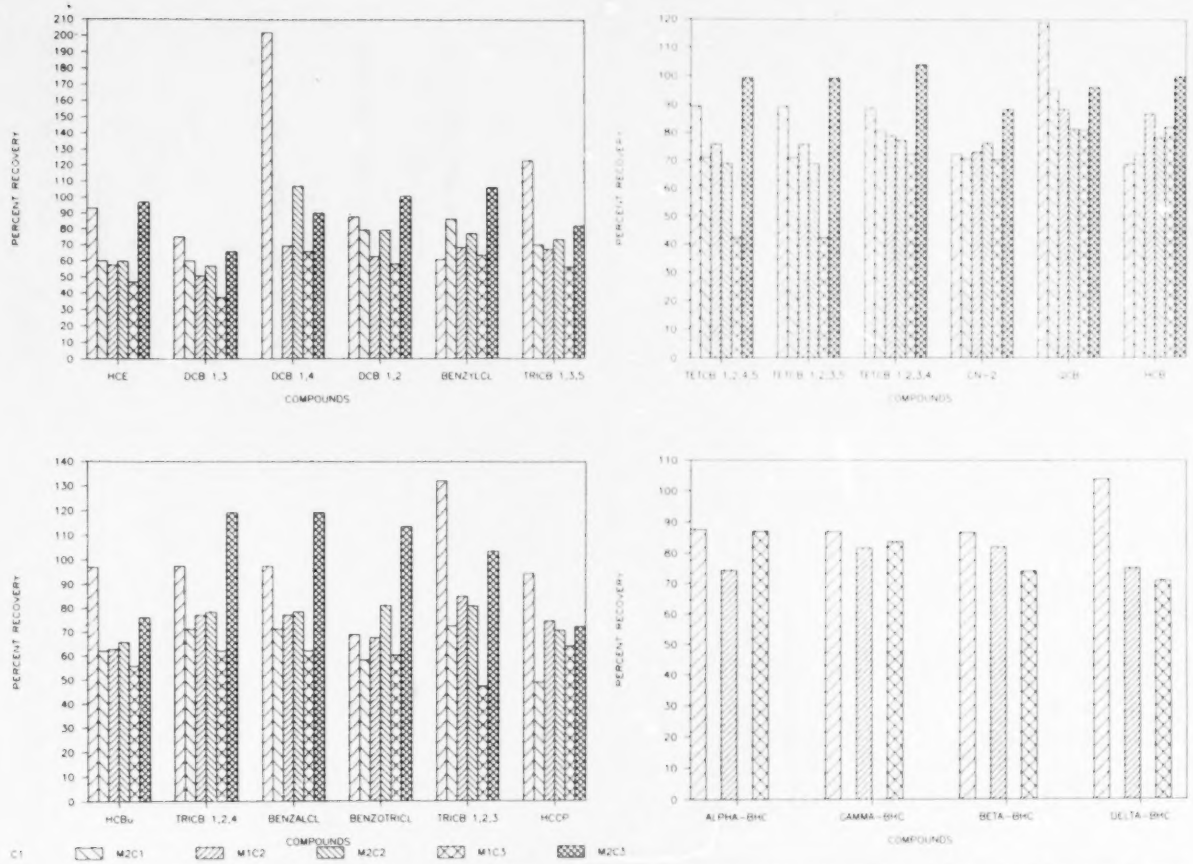

Figure 6. Distribution of average recoveries for Method 8120 compounds as a function of matrix and concentration (M1 is sample J; M2 is sample K; C1, C2, and C3 are 3 different concentrations at which the method was tested).

procedure, and the test compounds were eluted with 200 mL petroleum ether. Under these conditions, 15 compounds were eluted from the Florisil column, with recoveries greater than 78%, but no benzal chloride, benzotrichloride, or BHC isomers were recovered. When the method was modified by collecting a second fraction from the Florisil column, the BHC isomers were recovered quantitatively; however, benzal chloride and benzotrichloride were still not recovered.

Therefore, the Florisil procedure given in Method 3620, when modified by collecting an additional fraction, is satisfactory for all but 2 compounds. The relatively large volumes of solvents used in the Florisil cleanup step may increase the contamination of sample extracts by impurities in the solvents and, furthermore, the adsorbent materials are not recycled. Although they are not very expensive, the time required to prepare such materials, pack columns, elute the target analytes, and evaporate solvent contributes to the overall cost of analysis.

The use of commercially available disposable Florisil cartridges was, therefore, evaluated with the 22 target compounds to simplify the procedure, shorten the analysis time, and reduce the overall cost. With hexane or hexane–diethyl ether (1:1), the elution patterns of the BHC isomers were not reproducible and overall recoveries were not quantitative. When hexane–acetone (9:1) was used as eluant, recoveries were greater than 90% (except hexachlorobenzene at 78%), and the relative standard deviations of 5 determinations ranged between 0.4 and 6.5%, with most values less than 2%. Benzal chloride and benzotrichloride recoveries were 99 and 90%, respectively. This procedure was tested with several solid matrixes; the results are summarized in Table 3. More details on Florisil cartridge evaluation have been reported elsewhere (25).

Because of the superiority of Florisil cartridge chromatography over conventional Florisil cleanup (Method 3620), and because of the time and reagent savings (5 mL hexane–acetone for Florisil cartridge vs 200 mL petroleum ether for Method 3620), this procedure is recommended for incorporation in revised Method 8120.

Sample Preservation

Figures 3, 4, and 5 summarize the results of the preservation experiments at pH 7, 2, and 9, respectively. Recoveries were ≥80% on day 1 for all compounds at pH 7 but decreased to 50% on day 7. BHCs appeared to be stable for up to 21 days, while compounds such as benzyl chloride, benzal chloride, and benzotrichloride degraded rapidly. Recovery of benzal chloride on day 21 was slightly above 10%, and the recoveries of benzyl chloride and benzotrichloride were about 20%. Hexachlorobutadiene and hexachlorocyclopentadiene also degraded quite rapidly. The latter was reported to be very sensitive to sunlight (26). For example, in sunlight, the half-life of hexachlorocyclopentadiene is less than 3.5 min in aqueous solution and less than 1.6 and 2.5 min in hexane and methanol, respectively (26).

Benzyl chloride and benzotrichloride appeared to be slightly more stable at pH 2, and hexachlorobutadiene and hexachlorocyclopentadiene showed higher recoveries at pH 2 compared with pH 7. Recoveries of the rest of the compounds at pH 2 were not much different from those obtained at pH 7.

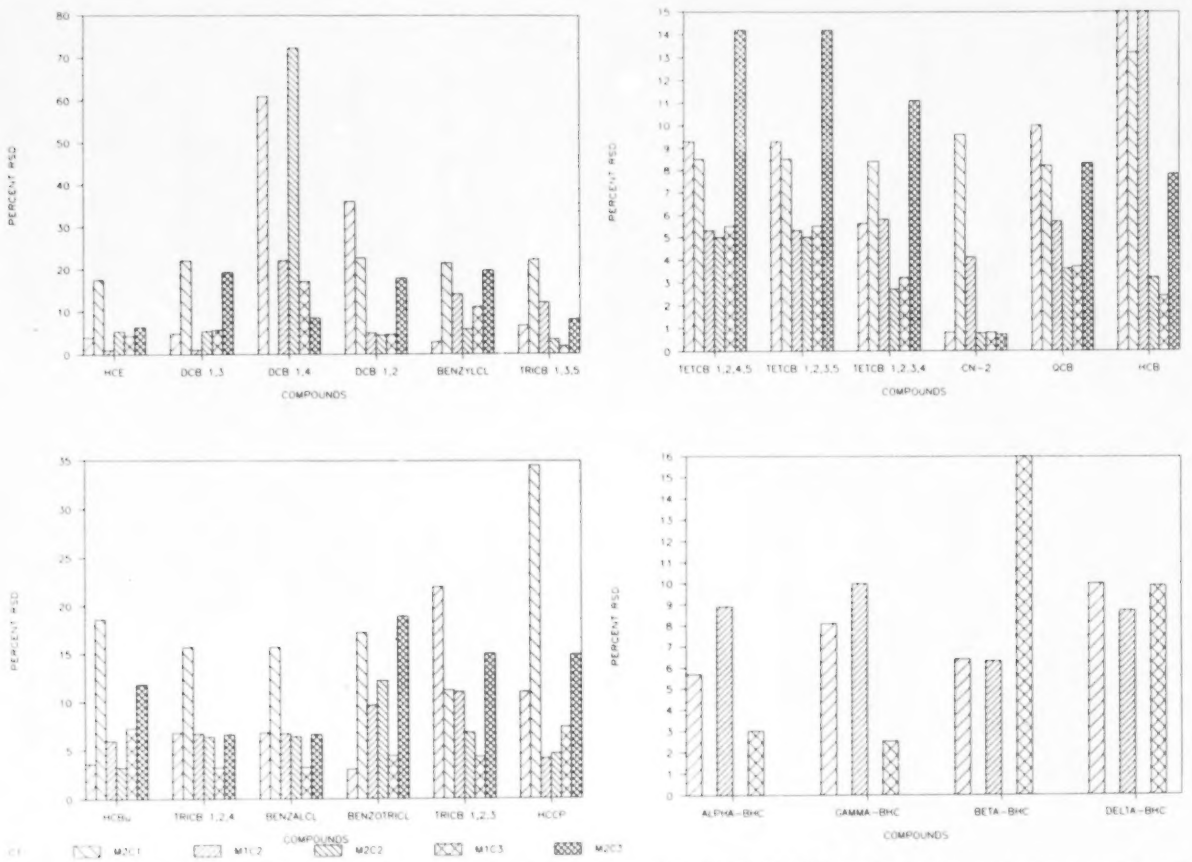

Figure 7. Distribution of relative standard deviations of average recoveries of Method 8120 compounds as a function of matrix and concentration (M1 is sample J; M2 is sample K; C1, C2, and C3 are 3 different concentrations at which the method was tested).

At pH 9, benzal chloride disappeared much faster than benzyl chloride or benzotrichloride. Among BHCs, only delta-BHC degraded. It is interesting to note that at pH 9, recovery of pentachlorobenzene was about 250% on day 7 and about 230% on day 14. At present, we do not know whether the increase in concentration of pentachlorobenzene is caused by pentachlorobenzene formation in the sample from other chlorinated hydrocarbons or by interference from another compound that might be coeluting with pentachlorobenzene on the DB-210 fused-silica open tubular column.

Method Performance

Method performance data are described in this paper as method precision, accuracy, and detection limit. Table 4 summarizes the results for 5 spiked reagent water samples which were extracted by Method 3510 and analyzed by GC/ECD using a DB-210 fused-silica open tubular column. The results from 2 soil samples (samples J and K) spiked at 4 concentrations, each in triplicate or quadruplicate, are presented in Figures 6 and 7, respectively. In the case of water samples, method precision is better than 9%, and compound recoveries (method accuracy) were greater than 87%. In the case of soil samples, method precision is better than 22% (except for 1,4-dichlorobenzene 1,2-dichlorobenzene, and hexachlorocyclopentadiene), and for most compounds, the recoveries were greater than 70%. Furthermore, the method recovery does not seem to be a function of the analyte concentration or the matrix.

The method detection limits (MDL) presented in Table 5 were determined by subjecting 7 reagent-grade water samples spiked with the 22 chlorinated hydrocarbons to the entire analytical process. The spiking levels of the 22 compounds were as follows: 2 ng/L for benzal chloride, hexachlorobutadiene, hexachlorocyclopentadiene, and hexachloroethane; 10 ng/L for benzotrichloride and hexachlorobenzene, 20 ng/L for BHC-isomers, pentachlorobenzene, tetrachlorobenzenes, and trichlorobenzenes; 200 ng/L for benzyl chloride, 1,2-dichlorobenzene, and 1,3-dichlorobenzene; 400 ng/L for 1,4-dichlorobenzene; and 1000 ng/L for 2-chloronaphthalene. Blank measurements were performed in triplicate. MDLs were determined from the standard deviations of the 7 replicates and the Student t-value for a one-tail test at the 99% confidence level (6 degrees of freedom). For waters, the MDLs ranged from 1.4 to 1300 ng/L. When using a 1.5 μL aliquot of 2 mL extract (after Florisil cleanup) obtained from 1 L of water containing the test compounds, the amounts injected into the GC column ranged from about 1 to 1000 pg. These amounts are sufficient for identifying the compounds because our lowest-level calibration standard used for quantifying the samples contained from 1 to 500 pg/μL, and we normally inject 1.5 μL aliquots. Detection limits lower than those given in Table 5 may be achievable with larger samples and by concentrating the extracts to 0.5 mL instead of 2 mL. An extract volume of 2 mL is suggested for Method 8120 because 1 mL is needed for the primary analysis; the other 1 mL must be saved for the confirmatory analysis.

Detection limits for soil and sediment samples need to be

Table 4. Accuracy and precision data for Methods 3510 and 8120 (without cleanup)

Compound	Added, µg/L	Av. rec. %[a,b]	Precision (RSD, %)
Benzal chloride[c]	10	95	3.0
Benzotrichloride	1.0	97	2.1
Benzyl chloride	100	90	6.2
2-Chloronaphthalene	200	91	6.5
1,2-Dichlorobenzene	100	92	5.7
1,3-Dichlorobenzene	100	87	8.7
1,4-Dichlorobenzene	100	89	8.9
Hexachlorobenzene	1.0	92	7.1
Hexachlorobutadiene	1.0	95	3.6
alpha-BHC	10	96	2.6
beta-BHC	10	103	3.6
gamma-BHC	10	96	2.8
delta-BHC	10	103	2.7
Hexachlorocyclopentadiene	10	97	5.1
Hexachloroethane	1.0	96	4.0
Pentachlorobenzene	1.0	89	6.5
1,2,3,4-Tetrachlorobenzene	10	96	3.4
1,2,4,5-Tetrachlorobenzene[d]	10	93	4.6
1,2,3,5-Tetrachlorobenzene[d]	10	94	6.0
1,2,4-Trichlorobenzene[c]	10	95	3.0
1,2,3-Trichlorobenzene	10	95	4.4
1,3,5-Trichlorobenzene	10	93	6.2
Surrogate recovery, %:			
α,2,6-Trichlorotoluene	1.0	85	6.5
1,4-Dichloronaphthalene	10	78	6.1
2,3,4,5,6-Pentachlorotoluene	1.0	80	5.9

[a] n = 5.
[b] Final extract volume is 10 mL.
[c,d] These compound pairs cannot be separated on the DB-210 column.

Table 5. Detection limits for Method 8120

Compound	MDL, ng/L[a]
Benzal chloride	2–5[b]
Benzotrichloride	6.0
Benzyl chloride	180
2-Chloronaphthalene	1,300
1,2-Dichlorobenzene	270
1,3-Dichlorobenzene	250
1,4-Dichlorobenzene	890
Hexachlorobenzene	5.6
Hexachlorobutadiene	1.4
alpha-BHC	11
beta-BHC	31
gamma-BHC	23
delta-BHC	20
Hexachlorocyclopentadiene	240
Hexachloroethane	1.6
Pentachlorobenzene	38
1,2,3,4-Tetrachlorobenzene	11
1,2,4,5-Tetrachlorobenzene	9.5
1,2,3,5-Tetrachlorobenzene	8.1
1,2,4-Trichlorobenzene	130
1,2,3-Trichlorobenzene	39
1,3,5-Trichlorobenzene	12

[a] MDL, method detection limit, was determined from analysis of 7 replicate aliquots of reagent water processed through entire analytical method (extraction, Florisil cleanup, and GC/EC analysis). MDL = $t_{n-(1,0.99)} \times$ SD where $t_{n-(1,0.99)}$ is the Student *t*-value appropriate for a 99% confidence interval and a standard deviation with n − 1 degrees of freedom, and SD is the standard deviation of 7 replicate measurements.
[b] Estimated from instrument detection limit.

determined on a case-by-case basis because of background contamination. Although revised Method 8120 suggests using from 10 to 35 g for solid matrixes, larger samples (e.g., 100 g) can be used if they are available to improve the method detection limits.

Conclusions

The method described here was tested with a few performance evaluation samples available from the Environmental Protection Agency. The results of these analyses indicate biases from −15 to +17% for alpha-BHC, gamma-BHC, 1,3,5- and 1,2,3-trichlorobenzene, and 1,2,4,5- and 1,2,3,4-tetrachlorobenzene. The bias is much higher for 1,4-dichlorobenzene when hexachloroethane is present in the sample, at the same concentration, because the 2 compounds give such different detector signals. Consequently, the sample extract requires several dilutions to bring the signal within the detector's linear range. Nonetheless, all Method 8120 compounds can be determined in the presence of other EPA base/neutral compounds and organochlorine pesticides. If the EPA priority pollutant acidic compounds are present, the Florisil procedure that uses a 1 g disposable cartridge and hexane–acetone (9:1) as the eluting solvent may be used to separate the Method 8120 compounds from the EPA priority pollutant phenols.

On the basis of the results of the experiments performed in this study, aqueous samples should be stored at 4°C in amber glass bottles, preferably with zero headspace, prior to extraction. Extraction should be performed within 72 h of sample collection.

Method 8120 has been revised and evaluated in a single-laboratory study with a few relevant environmental samples. The precision and accuracy of the results indicate that the revised method is reliable for determination of chlorinated hydrocarbons in liquid and solid matrixes. However, the revised method should be evaluated in an interlaboratory study and with additional environmental samples. This will help identify the applicability range and the limitations of the method and will define the interlaboratory method performance.

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